

Stoichiometric C=O Bond Oxidative Addition of Benzophenone by a Discrete Radical Intermediate To Form a Cobalt(I) Carbene

Seth L. Marquard, Mark W. Bezpalko, Bruce M. Foxman, and Christine M. Thomas*

Department of Chemistry, Brandeis University, 415 South Street, Waltham, Massachusetts 02454, United States

Supporting Information

ABSTRACT: Single electron transfer from the $\text{Zr}^{\text{III}}\text{Co}^0$ heterobimetallic complex $(\text{THF})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2$ (**1**) to benzophenone was previously shown to result in the isobenzopinacol product $[(\text{Ph}_2\text{CO})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2]_2$ (**2**) via coupling of two ketyl radicals. In this work, thermolysis of **2** in an attempt to favor a monomeric ketyl radical species unexpectedly led to cleavage of the C–O bond to generate a Zr/Co μ -oxo species featuring an unusual terminal $\text{Co}=\text{CPh}_2$ carbene linkage, $(\eta^2\text{-MesNP}^i\text{Pr}_2)_2\text{Zr}(\mu\text{-O})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}=\text{CPh}_2$ (**3**). This complex was characterized structurally and spectroscopically, and its electronic structure is discussed in the context of density functional theory calculations. Complex **3** was also shown to be active toward carbene group transfer (cyclopropanation), and silane addition to **3** leads to $\text{PhSiH}_2\text{O}-\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2$ (**5**) via a proposed Co–alkyl bond homolysis route.

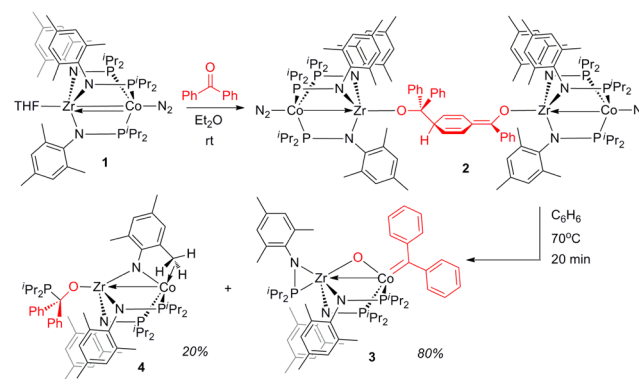
Although implicated as intermediates in a variety of C–C bond-forming reactions such as cyclopropanation, C–H functionalization, and Fischer–Tropsch (FT) synthesis,^{1–7} late first-row transition metal terminal carbene complexes without stabilizing heteroatom substituents are rare. First-row transition metal complexes featuring bridging alkylidene ligands are well-known,⁸ in contrast to their terminal counterparts. Structurally characterized terminal first-row transition metal carbenes include a nickel diphenylcarbene,⁹ copper diphenylcarbenes,^{10,11} and several examples of iron carbenes,^{12–16} including cycloheptatrienylidene,¹⁷ cyclobutenylidene,¹⁸ and cyclopropenylidene complexes.^{19,20} Noticeably absent from this list are cobalt carbenes, for which the only examples are the difluoro- and fluoro(perfluoroalkyl)carbenes recently reported by Baker and co-workers²¹ and those in which the carbene carbon is part of a metal-bound cyclopentadienyl ligand.^{22,23} Herein we report a rare example of a terminal cobalt carbene complex and its unusual synthesis via reductive C=O bond cleavage.

The cleavage of C–O multiple bonds is a relatively uncommon reaction despite being a proposed step in the FT process. Most proposed FT mechanisms proceed by cleavage of the $\text{C}\equiv\text{O}$ bond of carbon monoxide on metal surfaces (typically Fe or Co) followed by hydrogenation to afford metal–carbene intermediates that give rise to long-chain hydrocarbon products.^{5–7} Another example from organic synthesis is the McMurry reaction, which involves the reductive cleavage of ketones to olefins by mixtures of TiCl_3 and reducing

agents, possibly through carbenoid intermediates.²⁴ Tungsten complexes have been shown to undergo oxidative addition of the C=O bond of ketone substrates to afford $\text{W}(\text{oxo})$ -(carbene) species,^{25,26} and in another example, the C=O bond in a cyclopropanone derivative was added across a Zr–Fe bond, resulting in the formation of an iron carbene.¹⁹ A key step in the reduction of CO_2 to CO is C=O bond cleavage, and our group previously reported the facile cleavage of CO_2 by a Zr/Co heterobimetallic complex, resulting in a $\text{Zr}(\mu\text{-O})\text{Co}(\text{CO})$ complex.²⁷

In a recent publication on ketone hydrosilylation catalyzed by the heterobimetallic complex $(\text{THF})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2$ (**1**) (Mes = 2,4,6-trimethylphenyl),²⁸ we identified the tetrametallic isobenzopinacol-bridged complex **2** as the product of stoichiometric addition of benzophenone to **1** (Scheme 1).²⁹ In an attempt to probe for an equilibrium between **2** and a ketyl radical monomer, solutions of **2** were thermolyzed, leading to a C=O bond cleavage event.

Scheme 1



Thermolysis of a benzene solution of **2** at 70 °C for 1 h under N_2 afforded a red-brown solution containing two new paramagnetic complexes in a 4:1 ratio (Scheme 1). Fractional crystallization was used to separate these two compounds, and single-crystal X-ray diffraction determined the connectivity of these structural isomers to be $(\eta^2\text{-MesNP}^i\text{Pr}_2)_2\text{Zr}(\mu\text{-O})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}=\text{CPh}_2$ (**3**) and $\text{Ph}_2(\text{MesNP}^i\text{Pr}_2)\text{CO}-\text{Zr}(\mu\text{-NMes})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}$ (**4**). The structure of the minor red-orange complex **4** reveals this product to be the result of

Received: March 4, 2013

Published: April 5, 2013



homolysis of one of the amidophosphine ligands (see the Supporting Information).

The major product **3** has a characteristic paramagnetically broadened ^1H NMR spectrum with 18 distinct resonances, indicative of a complex with three inequivalent phosphinoamide ligands. Complex **3** was structurally identified as a terminal Co–diphenylcarbene complex featuring a μ -oxo ligand bridging Zr and Co (Figure 1A). This product presumably

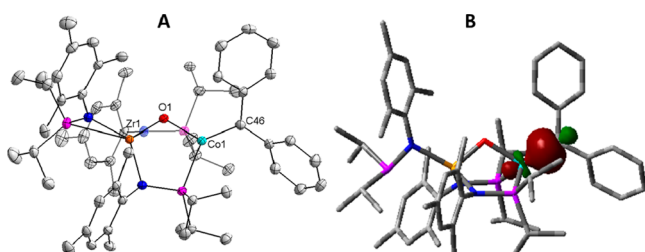


Figure 1. (A) ORTEP drawing of complex **3** with 50% probability ellipsoids. H atoms have been omitted for clarity. Selected bond lengths (Å): Co–C46, 1.906(2); Co–Zr, 3.0667(4); Zr–O1, 1.8459(16); Co–O1, 1.9710(16). (B) Computed NBO depicting the Co–C interaction in complex **3** (BP86/LANL2TZ(f)/6-311+G(d)/D95V).

results from cleavage of **2** into a radical monomer species followed by oxidative addition of the C–O bond. Complex **3** represents a rare structurally characterized non-heteroatom-stabilized cobalt carbene complex. The geometry about the carbene carbon (C46) is planar, consistent with sp^2 hybridization. The Co–C46 distance in **3** [1.906(2) Å] falls in the range of previously reported Fischer-type carbenes on cobalt (based on a 2013 search of the Cambridge Structural Database) but is considerably longer than the M–C distances in diphenylcarbene complexes of most other mid-to-late first-row transition metals (1.77–1.88 Å).^{9–11,13,14,30,31} Floriani's calix[4]arene-based $\text{Fe}=\text{CPh}_2$ systems are the only exceptions, although the long Fe–C distances in that case (~ 1.95 Å) were attributed to steric constraints.¹⁵ In the case of **3**, we postulate that the long Co–C46 distance might be attributed to the paramagnetic nature of the Co center, which inevitably leads to population of the metal–ligand antibonding orbitals. Indeed, complex **3** has a broad, paramagnetically shifted ^1H NMR spectrum and a solution magnetic moment of $3.1\mu_{\text{B}}$, consistent with an $S = 1$ complex.

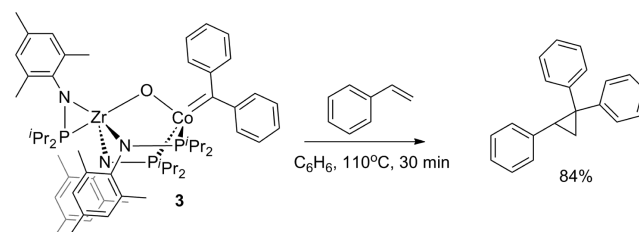
Several attempts were made to generate **3** via addition of diphenyldiazomethane to coordinatively unsaturated Zr/Co starting materials in an effort to circumvent the formation of byproduct **4**, but none of these routes proved successful. However, we found that **3** was formed exclusively (by ^1H NMR spectroscopy) when the labile N_2 ligand in **2** was removed in vacuo (generating $[(\text{Ph}_2\text{CO})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}]_2$ in situ) prior to thermolysis. The isolated yield of **3** was still fairly low because of the solubility of the complex in a wide variety of organic solvents, including hydrocarbons. Conversely, we considered that thermolysis of **2** under higher N_2 pressure might result in the exclusive formation of complex **4**. However, heating a benzene solution of **2** under 5 atm N_2 at 75°C for 2 h did not result in any conversion to either **3** or **4**. The results of these reactions imply that N_2 dissociation is necessary for the formation of both species. While no mechanistic data are available to suggest how **3** is formed from **2**, the eventual product of ketone C=O bond oxidative addition to **1** is

analogous to $(\eta^2\text{-MesNP}^i\text{Pr}_2)_2\text{Zr}(\mu\text{-O})(\text{MesNP}^i\text{Pr}_2)_2\text{Co-CO}$, the product of carbon dioxide C=O bond oxidative addition to **1**.²⁷ This observation permits speculation that a similar CO_2 -radical-based intermediate may be formed on the CO_2 activation reaction pathway.

Despite the absence of heteroatom donors to stabilize the carbene carbon, it was tempting to describe complex **3** as a $\text{Zr}^{\text{IV}}\text{Co}^{\text{I}}$ complex featuring a neutral singlet carbene by analogy to $(\eta^2\text{-MesNP}^i\text{Pr}_2)_2\text{Zr}(\mu\text{-O})(\text{MesNP}^i\text{Pr}_2)_2\text{Co-CO}$.²⁷ Further examination of **3** using density functional theory calculations revealed this to be the most accurate description. The geometry of **3** was optimized to a minimum, and the computed structure compared quite well with that determined experimentally using X-ray crystallography (see the Supporting Information). The distribution of the Mulliken spin density of **3** reveals little radical character on the carbene, in contrast to porphyrin-based cobalt carbenes reported in the literature.^{32,33} Complex **3** was unable to abstract a hydrogen atom from cyclohexadiene, providing experimental evidence for the lack of radical character on the carbene ligand. Natural bond orbital (NBO) calculations (Figure 1B) revealed a Co–C bond with significantly more carbon character (66.9%) than Co character (33.1%), and the carbene carbon's orbital contribution resembles that of an sp^2 -hybridized carbon atom (27.7% s, 72.3% p), suggesting that a dative donation of two electrons from carbon to cobalt is the best way to describe this interaction. Furthermore, the NBO calculations found no significant π interactions between the carbene carbon and cobalt. Consistent with this observation, the Wiberg bond index (WBI) for the Co–C_{carbene} bond was computed to be 0.77, compared with average WBIs of 0.46 and 0.49 for Co–P and Zr–N bonds, respectively, indicating a Co–C bond order between a single and double bond.

Metal carbenes generated via diazoalkane decomposition pathways are often proposed as intermediates in olefin cyclopropanation reactions, and cobalt-based catalysts using porphyrin^{32–34} and salen³⁵ ligand frameworks have been developed. To probe whether heterobimetallic complex **3** reacts with olefins in a similar manner, **3** was treated with styrene. After the reaction mixture was heated at 110°C for 30 min, (1,2-diphenylcyclopropyl)benzene was observed by GC/MS in 84% yield (Scheme 2). To probe whether this reaction

Scheme 2

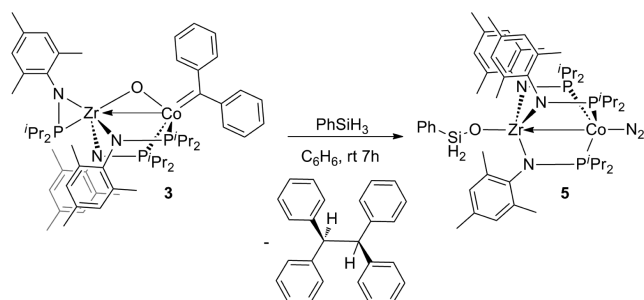


proceeds via carbene extrusion from **3** at elevated temperatures, the thermal stability of **3** was investigated. Upon thermolysis at 110°C in the absence of styrene, complex **3** decomposed to produce a mixture of tetraphenylethane, tetraphenylethylene, and diphenylmethane, suggesting that the $:\text{CPh}_2$ fragment is ejected at elevated temperatures. Moreover, monitoring the disappearance of carbene complex **3** by ^1H NMR spectroscopy in the absence or presence of styrene at 90°C revealed similar rates of reaction. Therefore, it is likely that cyclopropanation

proceeds via trapping of the extruded free diphenylcarbene fragment by styrene.

To explore the possibility that carbene complex **3** is a possible intermediate in our previously reported hydrosilylation chemistry,²⁹ the reaction of **3** with a silane was investigated. Allowing a benzene solution of complex **3** to react with phenylsilane at room temperature under N₂ afforded a new $S = 1/2$ complex identified as PhSiH₂O–Zr(MesNPⁱPr₂)₃Co–N₂ (**5**) (Scheme 3). ¹H NMR spectroscopy of **5** revealed nine

Scheme 3



paramagnetically broadened yet assignable resonances in the –2 to 8 ppm range, and the solution magnetic moment ($\mu_{\text{eff}} = 1.8\mu_B$) is consistent with a single unpaired electron. Single-crystal X-ray diffraction (see the Supporting Information) confirmed the structural connectivity and identity of **5** as a zirconium siloxide species analogous to the PhSiH₂O–Zr(MesNPⁱPr₂)₃Co(H)(CO) complex generated upon addition of PhSiH₃ to (η^2 -MesNPⁱPr₂)Zr(μ -O)(MesNPⁱPr₂)₂Co–CO.²⁷ Analysis of the crude reaction mixture by GC/MS indicated the formation of tetraphenylethane as the carbene-derived byproduct of this reaction. We previously reported that the CO₂ activation product (η^2 -MesNPⁱPr₂)Zr(μ -O)(MesNPⁱPr₂)₂Co–CO reacts readily with PhSiH₃ via Si–H addition across the Co–O bond to generate the hydrido/carbonyl complex PhSiH₂O–Zr(MesNPⁱPr₂)₃Co(H)(CO).²⁷ By extension, we propose that complex **3** initially reacts with phenylsilane to form a cobalt hydrido/carbene species. Subsequent insertion would afford a diphenylmethylcobalt complex, and homolysis of the Co^I–alkyl bond and dimerization of the resulting benzhydryl radical would form tetraphenylethane. Indeed, homolysis of cobalt–alkyl bonds has been studied extensively³⁶ and is known to occur in coenzyme B₁₂,³⁷ cobalt-catalyzed polymerization methods,³⁸ and cross-coupling reactions.³⁹ From the reaction of carbene complex **3** with phenylsilane, we can conclude that **3** does not play a role in the hydrosilylation of benzophenone, since the C–O bond cleavage appears to be irreversible.

In summary, we have shown that the highly polar metal–metal multiple bond in the reduced Zr/Co complex **1** facilitates the oxidative addition of the C=O bond in ketones. This particular route to a terminal carbene through a ketyl radical intermediate appears to be unique due to the inability to synthesize **3** via more traditional routes. Further study is required to determine whether this C=O bond cleavage is unique to benzophenone and other diaryl ketones and whether the C=O bond cleavage reaction reported herein is relevant to the mechanism of CO₂ activation. Future studies will also focus on further exploration of the reactivity and properties of carbene complex **3** and potential catalytic applications of this unique ketone activation.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, ¹H NMR spectra of **3**–**5**, computational details, X-ray crystallographic data collection and refinement details, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

thomasc@brandeis.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge financial support from the U.S. Department of Energy under Award DE-SC0004019. C.M.T. is grateful for a 2011 Sloan Research Fellowship. S.L.M. is grateful for a Camille and Henry Dreyfus Environmental Chemistry Fellowship.

■ REFERENCES

- (1) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271–288.
- (2) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348–356.
- (3) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417–424.
- (4) Warren, T. H.; Dai, X. Diketiminato Cu(I) and Co(I) Carbene Catalysts, and Cyclopropanation Methods Using Them. Pat. Appl. WO/2005/007659, 2005.
- (5) James, O. O.; Chowdhury, B.; Mesubi, M. A.; Maity, S. *RSC Adv.* **2012**, *2*, 7347–7366.
- (6) Corral Valero, M.; Raybaud, P. *Catal. Lett.* **2013**, *143*, 1–17.
- (7) Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M. *Top. Catal.* **2010**, *53*, 326–337.
- (8) Hahn, J. E. *Prog. Inorg. Chem.* **2007**, *31*, 205–264.
- (9) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 9976–9977.
- (10) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085–10094.
- (11) Hofmann, P.; Shishkov, I. V.; Rominger, F. *Inorg. Chem.* **2008**, *47*, 11755–11762.
- (12) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205.
- (13) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M.; You, X.-Z. *J. Am. Chem. Soc.* **2002**, *124*, 13185–13193.
- (14) Klose, A.; Hesschenbrouck, J.; Solari, E.; Latronico, M.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Organomet. Chem.* **1999**, *591*, 45–62.
- (15) Esposito, V.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *Inorg. Chem.* **2000**, *39*, 2604–2613.
- (16) Mahias, V.; Cron, S.; Toupet, L.; Lapinte, C. *Organometallics* **1996**, *15*, 5399–5408.
- (17) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2458–2460.
- (18) Bauer, D.; Harter, P.; Herdtweck, E. *J. Chem. Soc., Chem. Commun.* **1991**, 829–830.
- (19) Lutz, M.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. *Organometallics* **2001**, *20*, 2631–2634.
- (20) Dettlaf, G.; Hübener, P.; Klimes, J.; Weiss, E. *J. Organomet. Chem.* **1982**, *229*, 63–75.
- (21) Harrison, D. J.; Gorelsky, S. I.; Lee, G. M.; Korobkov, I.; Baker, R. T. *Organometallics* **2013**, *32*, 12–15.
- (22) Wadepohl, H.; Galm, W.; Pritzkow, H.; Wolf, A. *Chem.—Eur. J.* **1996**, *2*, 1453–1465.
- (23) Wadepohl, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 127–128.
- (24) Ephritikhine, M. *Chem. Commun.* **1998**, 2549–2554.
- (25) Chisholm, M. H.; Folting, K.; Kiang, J. A. *Organometallics* **1990**, *9*, 602–606.

- (26) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213–7214.
- (27) Krogman, J. P.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2011**, *133*, 14582–14585.
- (28) Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44–45.
- (29) Zhou, W.; Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Organometallics* **2013**, *32*, 1766–1772.
- (30) Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 327–352.
- (31) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978–2983.
- (32) Belof, J. L.; Cioce, C. R.; Xu, X.; Zhang, X. P.; Space, B.; Woodcock, H. L. *Organometallics* **2011**, *30*, 2739–2746.
- (33) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. J. *Am. Chem. Soc.* **2010**, *132*, 10891–10902.
- (34) Intrieri, D.; Caselli, A.; Gallo, E. *Eur. J. Inorg. Chem.* **2011**, 5071–5081.
- (35) Niimi, T.; Uchida, T.; Irie, R.; Katsuki, T. *Adv. Synth. Catal.* **2001**, *343*, 79–88.
- (36) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238–244.
- (37) Brown, K. L. *Chem. Rev.* **2005**, *105*, 2075–2150.
- (38) Smith, K. M.; McNeil, W. S.; Abd-El-Aziz, A. S. *Macromol. Chem. Phys.* **2010**, *211*, 10–16.
- (39) Ford, L.; Jahn, U. *Angew. Chem., Int. Ed.* **2009**, *48*, 6386–6389.